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(21) International Application Number: PCT/US99/08573 (22) International Filing Date: 19 April 1999 (19.04.99) (30) Priority Data: 09/072,059 4 May 1998 (04.05.98) US (71) Applicant: R.T. VANDERBILT COMPANY, INC. [US/US]; 30 Winfield Street, Norwalk, CT 06855 (US). (72) Inventor: SUHOZA, Richard, A.; 139 East Rocks Road, Norwalk, CT 06851 (US). (74) Agents: SORELL, Louis, S. et al.; Baker & Botts, LLP, 30 Rockefeller Plaza, New York, NY 10112-0228 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: STABILIZER COMPOSITIONS FOR POLYMERIC INSULATIONS (57) Abstract Polyethylene based compositions having incorporated a synergistic stabilizer consisting of zinc 2-mercaptotoluimidazole, zinc dibutyldithiocarbamate and tetrakis(methylene(3,5-di- <i>t</i> -butyl-4-hydroxyhydrocinnamate)) in critical ratios have improved resistance to oxidation and heat ageing. The polyethylene compositions can contain flame retardants, yellow pigments and fillers. The polyethylene compositions can be radiation or peroxide cross-linked to provide insulation for electrical conductors.		

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STABILIZER COMPOSITIONS FOR POLYMERIC INSULATIONS

The present invention concerns stabilizer systems for curable and cured polyolefin polymers. In particular the invention relates to stabilization of electrical polyolefin insulation against oxidation and thermal aging.

5 Cables, electrical wires and other electrical conductors are protected against exposure to extreme temperature variations, moisture and oil or chemical leaks by polymeric insulation. To be economical and practical, polymeric insulation used for electrical insulation must be durable and substantially retain its physical properties for effective and safe, long term performance.

10 Polyolefins are the base resins used for many electrical insulations. The most commonly used are polyethylene based resins. Polyethylenes are subject to oxidative degradation which is detrimental to the physical properties of the polymer causing embrittlement and cracking. The rate of oxidation degradation is greatly accelerated at elevated temperatures which are associated with electrical conductors. The oxidative
15 degradation is called "heat aging" when oxidation is accelerated or intensified by increased temperature.

It is known to stabilize polyolefins against heat aging with antioxidants. U.S. Pat. No. 4,260,661 discloses antioxidant combinations of zinc salt of mercaptoimidazole compounds, sterically hindered di-tert-butylphenol, and optionally zinc stearate, which are
20 particularly useful for stabilizing peroxide crosslinked polyolefins.

Besides peroxide cures, polyethylene is crosslinked with high energy radiation such as electron beam or x-rays. The crosslink during irradiation occurs at low temperature and thus, produces crosslinked structures of a different nature than peroxide cures. Therefore, the radiation crosslinked polyethylenes require particular heat aging stabilizers.

25 Surprisingly, it has been discovered that synergistic compositions of antioxidants prevent heat aging in polyethylene based resins, when radiation crosslinking is applied as well as during peroxide crosslinking.

SUMMARY OF THE INVENTION

According to the invention, there are provided polyethylene based compositions
30 stabilized against heat aging with a stabilizing amount of a synergistic stabilizer consisting of zinc 2-mercaptotoluimidazole, zinc dibutyldithiocarbamate and tetrakis (methylene (3,5-

di-t-butyl-4-hydroxyhydrocinnamate)) wherein the weight ratio of the imidazole to the dithiocarbamate to the cinnamate is from about 3.1:2.7:3.1 to about 3.9:3.3:3.9.

According to another aspect of the invention, there are provided electrical conductors insulated with a cured polyethylene based compound having improved heat aging stability and having incorporated therein a synergistic stabilizer consisting of zinc 2-mercaptotoluimidazole, zinc dibutyldithiocarbamate and tetrakis(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)) and optionally, a flame retardant and a yellow pigment or a filler.

Another object of the invention relates to a method of producing electrical conductors insulated with a polyethylene based compound by incorporating about 1 to 10 percent by weight a synergistic stabilizer described hereinabove and about 40 to 50 percent by weight of a flame retardant and a yellow pigment or a filler and crosslinking by radiation or peroxide-curing.

DETAILED DESCRIPTION OF THE INVENTION

The electrical insulations of the invention comprise ethylene based polymers, including homopolymers of ethylene and copolymers of ethylene with other polymerizable materials. The copolymers include, among others, ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, ethylene-vinyl acetate, ethylene-ethyl acrylate and ethylene-methyl acrylate copolymers. The polymers may be high, medium or low density. The insulations can be prepared from blends of such polymers and blends of polyethylene polymers with halogenated polyethylene polymers.

The synergistic stabilizer of the invention is composed of commercially available materials. The zinc 2-mercaptotoluimidazole is manufactured under the trade name VANOX®ZMTI and the zinc dibutyldithiocarbamate ingredient under the trade name BUTYL ZIMATE® by R.T. Vanderbilt Company, Inc. The tetrakis (methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)) is manufactured under the trade name Irganox® 1010 by Ciba Specialty Chemicals Corp.

The three component system displays synergistic stabilizing function when the components are present in the weight ratio of the imidazole to the dithiocarbamate to the cinnamate from about 3.1:2.7:3.1 to about 3.9:3.3:3.9, the preferred ratio being about 3.5:3.0:3.5.

The stabilizer of the invention may be incorporated in the polyethylene resin in an amount effective to produce the desired long range stability. Typically, an amount from

about 0.01 to 8.0 percent will be sufficient. A preferred range is from about 1.0 to 5.0 percent by weight based on hundred parts resin.

The polyethylene insulation is commonly cured by peroxide crosslinking. Common curing agents are dicumyl peroxide and tertiary diperoxides such as 2,5-dimethyl-2,5-di(t-butyl-peroxy)hexane, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexyne-3, n-butyl-4,4-bis(t-butylperoxy)valerate and the like. Peroxide curing is generally limited to low density polyethylene. The stabilizers of the invention provide good heat aging properties to peroxide-cured polyethylenes.

Alternately, polyethylenes are crosslinked by high energy radiation such as electron beam or x-rays. The advantage of radiation crosslinking is that it eliminates handling of peroxides. Additionally, the only by-products produced during curing in an inert atmosphere are hydrogen and low molecular weight hydrocarbons. The crosslinking during irradiation normally occurs at low temperature below the melting point of the polymer, while peroxide cured systems are crosslinked in the molten state. Ionizing radiation curing can be conducted with the use of triallyl cyanurate or ethylene dimethacrylate coagents.

The stabilizer system of the invention is particularly compatible with polyethylene based resins that are radiation cured at about 20 to 100°C. Alternately the stabilizers can be used in uncured polyethylene based resins.

The synergistic stabilizers of the invention are useful in polyethylene based formulations that contain yellow pigment concentrates. The yellow pigment concentrates usually contain chrome yellow and organic yellow pigments of the azo or non-azo type. Yellow pigment concentrates are incompatible with polyethylene based compounds and are known to exacerbate the deterioration of the polyethylene after crosslinking. The synergistic stabilizers counteract the negative action of the yellow pigment and increase the overall stability of the composition. Other applications include polyethyl based formulations that contain fillers. The fillers may be selected from carbon blacks such as furnace and thermal blacks and mineral fillers such as clay, calcium carbonate, talc, and silica. The fillers may contribute to viscosity control, thermal conductivity and control of thermal expansion of the insulation.

The stabilizers of the invention are compatible with conventional flame retardants. Typical flame retardants are halogen containing organic compounds and antimony compounds. Halogen containing compounds can be present up to 70 percent by weight per

hundred parts resin. Antimony oxide compounds can be present from about 35 to 70 parts by weight per hundred parts of polyethylene polymer. Particularly preferred flame retardants are aluminum hydroxide and alumina trihydrate, which display good arc and track resistance.

- 5 The solventless resins compounded with fillers, hardeners and other additives are used to encapsulate electronic components, insulate electrical cables, wires and conductors by casting, extruding and impregnation techniques.

 The data given hereinbelow are intended to illustrate, but not to limit the scope of the invention. Unless otherwise stated, all parts and percentages in the specification and
10 claims are expressed by weight.

EXAMPLE I

Static oven stability tests were conducted with crosslinked and non-crosslinked ethylene-vinyl acetate copolymer based resin (EVA) composition.

- The test samples were formulated with aluminum hydroxide flame retardant,
15 yellow pigment concentrate containing chrome yellow and diarylide yellow (Yellow 420 EVA, manufactured by Breen Color Concentrates, Inc.). Test sample 1 served as a control. To demonstrate synergism, test samples 2 to 4 and 7 to 9 contained the individual components of the present synergistic stabilizer and test samples 5 and 10 contained the three component stabilizer: zinc 2-mercaptotoluimidazole (hereinafter ZMTI), zinc
20 dibutyldithiocarbamate (hereinafter ZDTC) and tetrakis (methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)) (hereinafter cinnamate) in the weight ratio of 3.5:3.0:3.5. Test Samples 1 to 5 were not crosslinked, while test samples 6 to 10 were crosslinked with dicumyl peroxide.

- The test ingredients were weighed and thoroughly blended before milling at 99 to
25 102°C for 5 to 10 minutes. After milling, 3 x 5 x 0.003 inch specimens were cut and placed on aluminum foil. The specimens were placed in a forced air circulating oven that was preheated to 204°C. Samples were taken until total degradation occurred as evidenced by dark brown or black color of the aged specimen.

- The data are compiled in Table I herein. The results show the superior synergistic
30 effect of samples 5 and 10 containing the stabilizer of the invention in crosslinked and non-crosslinked EVA polymer.

TABLE I

Compositions, Parts

<u>Components</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
EVA	50	50	50	50	50	50	50	50	50	50
5 Al hydroxide	50	50	50	50	50	50	50	50	50	50
Yellow 420	2	2	2	2	2	2	2	2	2	2
Dicumyl peroxide						3	3	3	3	3
Cinnamate		3					3			
10 ZDTC			3					3		
ZMTI				3					3	
Stabilizer					3					3
Oven Aged at 204°C										
15 Hours to Complete										
Degradation:	8	32	16	32	280	8	32	16	32	265

EXAMPLE 2

The stability of non-crosslinked polyethylene (PE) based resin composition was tested by determining the oxygen induction time by differential scanning calorimetry.

The test samples were formulated with carbon black filler. Test sample 11 served
5 as a control. To demonstrate synergism, test samples 12 to 14 contained the individual components for the present stabilizer described in Example 1 above. Test samples 15 and 16 contained the three component stabilizer.

The test sample sheets were placed into a tared aluminum sample pan, weighed and loaded into Differential Scanning Calorimeter, (DSC) TA Instruments Model 2910 along
10 with an empty pan as reference. The cell of DSC was purged isothermally with nitrogen for 5 minutes. The cell was heated at a programmed ramped rate of 20° min. to 230°C. After equilibrating the instrument, oxygen was introduced and the test was run at 230°C until onset point time (OIT) is reached, i.e., point value time signal is obtained.

The data are compiled in Table II. The results show the superior synergistic effect
15 of samples 15 and 16 containing the stabilizer of the invention in polymers containing carbon black with and without a flame retardant.

TABLE II

Compositions, Parts

<u>Components</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>
PE	95	95	95	95	95	95
5 Carbon black	5	5	5	5	5	5
Al hydroxide	--	--	--	--	--	10
Cinnamate	--	3	--	--	--	--
ZDTC	--	--	3	--	--	--
ZMTI	--	--	--	3	--	--
10 Stabilizer	--	--	--	--	3	3
Onset Point Time, min.	3.08	28.04	51.06	3.02	93.04	91.43

The above embodiments and illustrations have shown various aspects of the present invention. Other variations will be evident to those skilled in the art and such modifications are intended to be within the scope of the invention as defined in the appended claims.

What is claimed is:

1. A polyethylene based composition curable by radiation crosslinking or peroxide comprising a major amount of at least one ethylene containing polymer and a minor heat aging inhibiting amount of a synergistic stabilizer composition consisting of zinc 2-
5 mercaptotoluimidazole, zinc dibutyldithiocarbamate and tetrakis(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)) wherein the weight ratio of the imidazole to the dithiocarbamate to the cinnamate is from about 3.1:2.7:3.1 to about 3.9:3.3:3.9.
2. The polyethylene based composition according to claim 1 wherein the ethylene containing polymer is selected from polyethylene, copolymers of ethylene and other
10 polymerizable hydrocarbons, halogen containing polyethylene and blends thereof.
3. The polyethylene based composition according to claim 1 which further contains a filler.
4. The polyethylene based composition according to claim 1 which further contains carbon black.
- 15 5. A curable, flame retardant insulating compositions comprising
 - (a) an ethylene containing polymer,
 - (b) a flame retardant selected from antimony compounds and halogen compounds,
 - (c) a synergistic stabilizer composition consisting of zinc 2-mercapto-
20 toluimidazole, zinc dibutyldithiocarbamate and tetrakis(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)) wherein the ratio of the imidazole to the dithiocarbamate to the cinnamate is about 3.1:2.7:3.1 to 3.9:3.3:3.9.
6. The insulating composition according to claim 5 wherein the flame retardant is
25 alumina trihydrate.
7. The insulating composition according to claim 5 wherein the flame retardant is aluminum hydroxide.
8. The insulating composition of claim 5 which further contains yellow pigments.
9. The insulating composition of claim 5 which further contains a filler.
- 30 10. The insulating composition of claim 5 which further contains carbon black.
11. The cured composition of claim 5 which is crosslinked by radiation crosslinking.

10. The insulating composition of claim 5 which further contains carbon black.
11. The cured composition of claim 5 which is crosslinked by radiation crosslinking.
12. The cured composition of claim 5 which is crosslinked with organic peroxide.
- 5 13. A method of improving the heat aging stability of cured ethylene polymer containing compositions comprising the steps of combining with a curable ethylene containing polymer a synergistic stabilizer composition consisting of zinc-2-mercaptotoluimidazole, zinc dibutyldithiocarbamate and tetrakis(methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)) in the amount of about 1 to 10 parts per hundred parts by
10 weight of polymer and crosslinking the polymer by radiation crosslinking or peroxide crosslinking.
14. A method according to claim 13 wherein the polymer compositions contains a flame retardant.
- 15 15. A method according to claim 13 wherein the polymer compositions contain yellow pigments.
16. A method according to claim 13 wherein the polymer compositions contain a filler.
17. A method according to claim 13 wherein the polymer compositions contain carbon black.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/08573

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K5/134 C08K5/14 C08K5/37 C08K5/39 C08L23/04
H01B3/44

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B. FIELDS SEARCHED

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IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 260 661 A (WALTERS ET AL.) 7 April 1981 (1981-04-07) cited in the application claims 1,2,8; tables I,II,III ---	1,4,5,10
A	US 4 382 112 A (BETTS ET AL.) 3 May 1983 (1983-05-03) claims 1,5; table I ---	1,5,12
A	EP 0 513 699 A (HIMONT INC.) 19 November 1992 (1992-11-19) page 5, paragraph 3 - paragraph 4 examples 1-3,C2,C3; table 1 ---	1,13
A	EP 0 206 413 A (BOZZETTO) 30 December 1986 (1986-12-30) claims 1,4,5,9 ---	1,13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 530 641 A (GEN. ELECTRIC) 10 March 1993 (1993-03-10) example 1; table 1 ----	1, 13
A	EP 0 254 010 A (SUMITOMO) 27 January 1988 (1988-01-27) claims 1,4; examples ----	1, 4
A	DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class A17, AN 70-04345R XP002111210 & JP 45 000280 B (MITSUBISHI RAYON CO LTD) abstract -----	1, 13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/08573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4260661 A	07-04-1981	NONE	
US 4382112 A	03-05-1983	NONE	
EP 513699 A	19-11-1992	US 5196462 A AT 156849 T AU 662523 B AU 1628992 A CA 2067656 A CN 1066666 A CS 9201481 A DE 69221533 D DE 69221533 T DK 513699 T HU 66133 A JP 5179084 A MX 9202227 A	23-03-1993 15-08-1997 07-09-1995 19-11-1992 17-11-1992 02-12-1992 18-11-1992 18-09-1997 29-01-1998 01-09-1997 28-09-1994 20-07-1993 01-11-1993
EP 206413 A	30-12-1986	DK 281086 A FI 862524 A GR 861550 A JP 62043437 A PT 82790 A,B	20-12-1986 20-12-1986 10-10-1986 25-02-1987 01-07-1986
EP 530641 A	10-03-1993	US 5158997 A AT 148903 T AU 655296 B AU 2122692 A CA 2077110 A CN 1070204 A DE 69217434 D DE 69217434 T DK 530641 T FI 923894 A JP 5194803 A MX 9204985 A RU 2066333 C ZA 9206338 A	27-10-1992 15-02-1997 15-12-1994 04-03-1993 01-03-1993 24-03-1993 27-03-1997 26-06-1997 07-04-1997 01-03-1993 03-08-1993 01-02-1993 10-09-1996 22-04-1993
EP 254010 A	27-01-1988	CA 1295073 A DE 3781476 A JP 2091969 C JP 7119285 B JP 63099239 A KR 9503266 B US 4983685 A	28-01-1992 08-10-1992 18-09-1996 20-12-1995 30-04-1988 07-04-1995 08-01-1991
JP 45000280 B		NONE	